

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 August 2003 (07.08.2003)

PCT

(10) International Publication Number
WO 03/064342 A1

(51) International Patent Classification⁷: **C03C 3/087**,
3/095

(21) International Application Number: PCT/US03/02388

(22) International Filing Date: 28 January 2003 (28.01.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/056,051 28 January 2002 (28.01.2002) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE,
SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC,
VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI,
SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN,
GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: CLEAR GLASS COMPOSITION

(57) Abstract: Glass is provided so as to have high visible transmission and/or fairly clear or neutral color. In certain example embodiments of making glass according to examples of the invention, the glass batch may include a base glass (e.g., soda lime silica base glass) and, in addition, by weight percentage: total iron (expressed as Fe₂O₃): 0.01 to 0.30%, erbium oxide (e.g., Er₂O₃): 0.01 to 0.30%, cerium oxide (e.g., CeO₂): 0.005 to 0.30%. Optionally, neodymium oxide (e.g., Nd₂O₃) may also be provided in the glass in certain example embodiments. In other embodiments, the cerium oxide may be replaced with or supplemented by NaNO₃ or some other nitrate(s) as an oxidizer.

WO 03/064342 A1

CLEAR GLASS COMPOSITION

This invention relates to glass compositions and methods of making the same. More particularly, this invention relates to glass having high light transmittance in the visible range and/or fairly neutral color. Such glass compositions are thus useful, for example, in architectural windows, patterned glass applications, solar cells, and/or automotive windows.

BACKGROUND OF THE INVENTION

Glass that is fairly clear in color and highly transmissive to visible light (e.g., at least 75% transmissive, or even more preferably at least 80% transmissive) is sometimes desirable. One way of achieving such as glass is to use very pure base glass materials (e.g., substantially free of colorants such as iron). However, base materials with a high degree of purity are expensive and thus not always desirable and/or convenient. In other words, for example, the removal of iron from glass raw materials has certain practical and/or economical limits.

As can be appreciated from the above, glass raw materials (e.g., silica, soda ash, dolomite, and/or limestone) typically include certain impurities such as iron. The total amount of iron present is expressed herein in terms of Fe_2O_3 in accordance with standard practice. However, typically, not all iron is in the form of Fe_2O_3 . Instead, iron is usually present in both the ferrous state (Fe^{2+} ; expressed herein as FeO , even though all ferrous state iron in the glass may not be in the form of FeO) and the ferric state (Fe^{3+}). Iron in the ferrous state (Fe^{2+} ; FeO) is a blue-green colorant, while iron in the ferric state (Fe^{3+}) is a yellow-green colorant. The blue-green colorant of ferrous iron (Fe^{2+} ; FeO) is of particular concern when seeking to achieve a fairly clear or neutral colored glass, since as a strong colorant it introduces significant color into the glass. While iron in the ferric state (Fe^{3+}) is also a colorant, it is of less concern when seeking to achieve a glass fairly clear in color since iron in the ferric state tends to be weaker as a colorant than its ferrous state counterpart.

In view of the above, it is apparent that there exists a need in the art for a new glass composition which enables a glass to have fairly clear color and/or high visible transmission, without having to resort to extremely pure (i.e., free of iron) glass raw materials.

5

SUMMARY OF THE INVENTION

An object of this invention is to provide a glass that has fairly clear color and/or high visible transmission.

Another object of this invention is to provide a glass having a visible transmission of at least 75% (more preferably at least 80%, and most preferably at least 10 85%), wherein in making the glass a batch therefor includes a base glass (e.g., soda lime silica glass) and in addition comprising (or consisting essentially of in certain embodiments), by weight percentage:

	total iron (expressed as Fe_2O_3):	0.01 to 0.30 %
	erbium oxide (e.g., Er_2O_3):	0.01 to 0.30 %
15	cerium oxide (e.g., CeO_2):	0.005 to 0.30 %.

Optionally, other colorants such as neodymium oxide (e.g., Nd_2O_3) may also be provided in certain example embodiments. While cerium oxide is preferred in many embodiments, its presence is not a requirement. In other embodiments of this invention, the cerium oxide (e.g., CeO_2) in the glass batch may be either replaced or 20 supplemented by sodium nitrate (NaNO_3) as an oxidizer.

Another object of this invention is to fulfill one or more of the above-listed objects and/or needs.

Certain example embodiments of the invention fulfill one or more of the above-listed objects and/or needs by providing a method of making glass, the method 25 comprising:

providing a glass batch comprising:

	Ingredient	wt. %
	SiO ₂	67 – 75 %
	Na ₂ O	10 – 20 %
	CaO	5 – 15 %
5	MgO	0 – 5 %
	Al ₂ O ₃	0 – 5 %
	K ₂ O	0 – 5 %
	total iron (expressed as Fe ₂ O ₃)	0.01 to 0.30 %
	erbium oxide	0.01 to 0.30 %
10	cerium oxide and/or a nitrate	0.005 to 2.0 %
	neodymium oxide	0 to 0.15 %

melting the batch and forming a resulting glass that has visible transmission of at least 75%, a transmissive a* color value of -1.0 to +1.0, and a transmissive b* color value of -1.0 to +1.5.

15 Certain other example embodiments of this invention fulfill one or more of the above-listed objects and/or needs by providing a glass comprising:

total iron (expressed as Fe ₂ O ₃)	0.01 to 0.30 %
erbium oxide	0.01 to 0.30 %
cerium oxide	0.005 to 0.30 %.

20 Certain other example embodiments of this invention fulfill one or more of the above-listed objects and/or needs by providing a method of making glass, the method comprising providing a glass batch comprising:

total iron (expressed as Fe ₂ O ₃):	0.01 to 0.30 %
erbium oxide:	0.01 to 0.30 %

cerium oxide and/or a nitrate: 0.005 to 2.0 %, and
using the glass batch to make glass.

Certain other example embodiment of this invention fulfill one or more of the above-listed objects and/or needs by providing a glass comprising:

5 total iron (expressed as Fe_2O_3) 0.01 to 0.30 %, and
erbium oxide 0.01 to 0.30 %.

DETAILED DESCRIPTION OF CERTAIN EMBODIMENTS OF THIS INVENTION

Glasses according to different embodiments of this invention may be used, for
10 example, in the automotive industry (e.g., windshields, backlites, side windows, etc.), in architectural applications, for patterned glass applications, solar cell applications, and/or in other suitable applications.

Certain glasses according to this invention utilize soda-lime-silica flat glass as their base composition/glass. In addition to base composition/glass, a unique colorant
15 portion is provided in order to achieve a glass that is fairly clear in color and/or has a high visible transmission. An exemplary soda-lime-silica base glass according to certain embodiments of this invention, on a weight percentage basis, includes the following basic ingredients:

TABLE 1: EXAMPLE BASE GLASS

20	Ingredient	Wt. %
	SiO_2	67 – 75 %
	Na_2O	10 – 20 %
	CaO	5 – 15 %
	MgO	0 – 5 %
25	Al_2O_3	0 – 5 %
	K_2O	0 – 5 %

BaO

0 – 1 %

Other minor ingredients, including various conventional refining aids, such as SO_3 , carbon, and the like may also be included in the base glass. In certain embodiments, for example, glass herein may be made from batch raw materials silica sand, soda ash, dolomite, limestone, with the use of salt cake (SO_3) and/or Epsom salts (e.g., about a 1:1 combination of both) as refining agents. Preferably, soda-lime-silica based glasses herein include by weight from about 10-15% Na_2O and from about 6-12% CaO . While a soda-lime-silica base glass set forth above is preferred in certain embodiments of this invention, this invention is not so limited. Thus, other base glasses (e.g., borosilicate glass) may instead be employed in alternative embodiments of this invention.

In addition to the base glass (e.g., see Table 1 above), in making glass according to the instant invention the glass batch includes materials (including colorants and/or oxidizers) which cause the resulting glass to be fairly neutral in color and/or have a high visible light transmission. These materials may either be present in the raw materials (e.g., small amounts of iron), or may be added to the base glass materials in the batch (e.g., cerium, erbium, etc.). In certain preferred embodiments, the resulting glass has visible transmission of at least 75%, more preferably at least 80%, and most preferably at least 85%.

In certain embodiments of this invention, in addition to the base glass, the glass batch includes materials as set forth in Table 2 below (in terms of weight percentage of the total glass composition):

TABLE 2: EXAMPLE GLASS BATCH OF FIRST EMBODIMENT

Ingredient	General (Wt.%)	More Preferred	Most Preferred
total iron (expressed as Fe_2O_3):	0.01 – 0.30 %	0.02 – 0.20 %	0.03 – 0.15 %
erbium oxide (e.g., Er_2O_3):	0.01 – 0.30 %	0.02 – 0.20 %	0.03 – 0.13 %
cerium oxide (e.g., CeO_2):	0.005 – 0.30 %	0.01 – 0.18 %	0.03 – 0.12 %

The batch is melted and glass formed using the known float process. Optionally, in certain example embodiments of the invention, neodymium oxide (e.g., Nd_2O_3) may be added to the batch, as exemplified below in Table 3 according to a second example embodiment of this invention (the material listed in Table 3 are in addition to the base glass described above).

TABLE 3: EXAMPLE GLASS BATCH OF SECOND EMBODIMENT

Ingredient	General (Wt.%)	More Preferred	Most Preferred
total iron (expressed as Fe_2O_3):	0.01 – 0.30 %	0.02 – 0.20 %	0.03 – 0.15 %
erbium oxide (e.g., Er_2O_3):	0.01 – 0.30 %	0.02 – 0.20 %	0.03 – 0.13 %
10 cerium oxide (e.g., CeO_2):	0.005 – 0.30 %	0.01 – 0.18 %	0.03 – 0.12 %
neodymium oxide (e.g., Nd_2O_3):	0.005 – 0.15 %	0.010 – 0.050%	0.010-0.030%

In certain embodiments of this invention (e.g., first and/or second embodiments above), the colorant portion is substantially free of other colorants (other than potentially trace amounts). However, it should be appreciated that amounts of other materials (e.g., refining aids, melting aids, colorants and/or impurities) may be present in the glass in certain other embodiments of this invention without taking away from the purpose(s) and/or goal(s) of the instant invention. It is noted that while the presence of cerium oxide is preferred in many embodiments of this invention, it is not required in all embodiments. Moreover, it is possible to use little or no Er in certain embodiments of this invention.

In other embodiments of this invention, the cerium oxide (e.g., CeO_2) may be either replaced or supplemented by NaNO_3 in the glass batch; see the third, fourth and fifth embodiments below (the batch materials in Tables 4-6 below are in addition to the base glass raw materials described above).

TABLE 4: EXAMPLE GLASS BATCH OF THIRD EMBODIMENT

Ingredient	General (Wt.%)	More Preferred	Most Preferred
total iron (expressed as Fe_2O_3):	0.01 – 0.30 %	0.02 – 0.20 %	0.03 – 0.15 %
erbium oxide (e.g., Er_2O_3):	0.01 – 0.30 %	0.02 – 0.20 %	0.03 – 0.13 %
5 sodium nitrate (NaNO_3):	0.1 – 2.0 %	0.2 – 1.5 %	0.3 – 1.2 %

TABLE 5: EXAMPLE GLASS BATCH OF FOURTH EMBODIMENT

Ingredient	General (Wt.%)	More Preferred	Most Preferred
total iron (expressed as Fe_2O_3):	0.01 – 0.30 %	0.02 – 0.20 %	0.03 – 0.15 %
erbium oxide (e.g., Er_2O_3):	0.01 – 0.30 %	0.02 – 0.20 %	0.03 – 0.13 %
10 sodium nitrate (NaNO_3):	0.1 – 2.0 %	0.2 – 1.5 %	0.3 – 1.2 %
neodymium oxide (e.g., Nd_2O_3):	0.005 – 0.15 %	0.010 – 0.050 %	0.010-0.030 %

TABLE 6: EXAMPLE GLASS BATCH OF FIFTH EMBODIMENT

Ingredient	General (Wt.%)	More Preferred	Most Preferred
total iron (expressed as Fe_2O_3):	0.01 – 0.30 %	0.02 – 0.20 %	0.03 – 0.15 %
15 erbium oxide (e.g., Er_2O_3):	0.01 – 0.30 %	0.02 – 0.20 %	0.03 – 0.13 %
cerium oxide (e.g., CeO_2):	0 – 0.30 %	0 – 0.18 %	0 – 0.12 %
sodium nitrate (NaNO_3):	0 – 2.0 %	0.2 – 1.5 %	0.3 – 1.2 %

In the fifth embodiment (see Table 6 above), cerium oxide (e.g., CeO_2) and sodium nitrate (NaNO_3) may be combined as oxidizers, so as to cause the effects of equations (1) and (2) below. Accordingly, one or both of cerium oxide and/or sodium nitrate may be provided in this fifth embodiment.

It is noted that in certain embodiments herein, the amount of total iron may even be less than 0.10 %.

The above batches are melted and the float process used to form glass (e.g., soda lime silica glass) in a known manner.

The total amount of iron present in the glass batch and in the resulting glass, i.e., in the colorant portion thereof, is expressed herein in terms of Fe_2O_3 in accordance with standard practice. This, however, does not imply that all iron is actually in the form of Fe_2O_3 (see discussion above in this regard). Likewise, the amount of iron in the ferrous state (Fe^{+2}) is reported herein as FeO , even though all ferrous state iron in the glass batch or glass may not be in the form of FeO . As mentioned above, iron in the ferrous state (Fe^{2+} ; FeO) is a blue-green colorant, while iron in the ferric state (Fe^{3+}) is a yellow-green colorant; and the blue-green colorant of ferrous iron is of particular concern, since as a strong colorant it introduces significant color into the glass which can sometimes be undesirable when seeking to achieve a neutral or clear color.

According to certain example embodiments of this invention, the presence of cerium oxide (e.g., CeO_2) as an oxidizer in the glass batch acts as a chemical decolorizer since during melting of the glass batch it causes iron in the ferrous state (Fe^{2+} ; FeO) to oxidize to the ferric state (Fe^{3+}) as illustrated by the following equation:

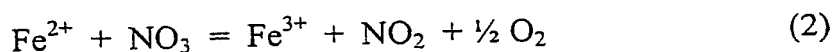


Equation (1) shows that the presence of cerium oxide in the glass batch causes an amount of the strong blue-green colorant of ferrous iron (Fe^{2+} ; FeO) to oxidize into the weaker yellow-green ferric iron colorant (Fe^{3+}) during the glass melt (note: some ferrous state iron will usually remain in the resulting glass, as potentially may some Ce^{4+}). Accordingly, a significant portion of the CeO_2 added to the original glass batch prior to the melt is transformed during the melt into Ce_2O_3 which is present in the resulting glass. The aforesaid oxidation of the iron tends to reduce coloration of the glass, and does not significantly decrease visible light transmission of the resulting glass (in certain instances, this may even causes visible transmission to increase). However, those of skill in the art will appreciate that there still exists significant coloration in the glass due to the ferric iron if only the iron and cerium oxide are provided. In other words, it has been found that adding cerium oxide to only iron

containing glass is not sufficient to achieve a desired fairly clear or neutral color.

It is noted that, like Fe_2O_3 , the phrase "cerium oxide" as used herein refers to total cerium oxide (i.e., including cerium oxide in both the Ce^{4+} and Ce^{3+} states).

As mentioned above, the cerium oxide may be replaced by, or supplemented
5 with, sodium nitrate in certain example embodiments of this invention. In
embodiments where sodium nitrate (NaNO_3) is provided in the glass (e.g., see Tables 3-
5 above), it functions in a manner similar to cerium oxide as shown in the below
equation (but note the potential for oxygen bubbles). In particular, like cerium oxide,
sodium nitrate can be added to the glass batch as an oxidizer to cause an amount of the
10 strong blue-green colorant of ferrous iron (Fe^{2+} ; FeO) to oxidize into the weaker yellow-
green ferric iron colorant (Fe^{3+}) during the glass melt (note: some ferrous state iron will
usually remain in the resulting glass):



Those skilled in the art will recognize that the most of the nitrate (e.g., sodium
15 nitrate) added to the glass batch decomposes during the melt so that some burns off as
 NO_x while other parts of it end up in the glass as Na_2O . While sodium nitrate (NaNO_3)
is utilized as an oxidizer in Tables 4-6 above, the instant invention is not so limited.
For example, other nitrates (e.g., potassium nitrate KNO_3 , or any other suitable nitrate)
may be used instead of or in addition to sodium nitrate in alternative embodiments of
20 this invention.

In order to compensate for the color caused by the ferric iron resulting from the
addition of the cerium oxide and/or sodium nitrate, it has been found that adding
erbium oxide (e.g., Er_2O_3 or any other suitable stoichiometric form) and/or neodymium
oxide (e.g., Nd_2O_3 of any other suitable stoichiometric form) causes the color of the
25 resulting glass to become more clear (i.e., more neutral as the a^* and/or b^* color
value(s) move(s) toward neutral 0). Erbium oxide acts as a pink colorant, while
neodymium oxide acts as a purple colorant. One or both of Er and/or Nd apparently
acts to physically compensate for the iron color, thereby making the color of the glass

more neutral which is desirable in certain embodiments of this invention, while enabling the glass to still have high visible transmission.

It will be appreciated by those skilled in the art that the addition of cerium oxide and/or sodium nitrate (see equations (1) and (2) above) results in a glass with a lower "redox" value (i.e., less iron in the ferrous state FeO). In this regard, the proportion of the total iron in the ferrous state (FeO) is used to determine the redox state of the glass, and redox is expressed as the ratio $\text{FeO} / \text{Fe}_2\text{O}_3$, which is the weight percentage (%) of iron in the ferrous state (FeO) divided by the weight percentage (%) of total iron (expressed as Fe_2O_3) in the resulting glass. Due to the presence of the cerium oxide and/or sodium nitrate, the redox of glass according to certain example embodiments of this invention is rather low; in particular, glass according to certain example embodiments of this invention may have a redox value (i.e., $\text{FeO} / \text{Fe}_2\text{O}_3$) of less than or equal to 0.25, more preferably less than or equal to 0.20; even more preferably less than or equal to 0.15, and most preferably less than or equal to 0.13. Moreover, resulting glass according to certain example embodiments of this invention may include iron in the ferrous state (FeO) in an amount (wt. %) of less than or equal to 0.020 %, more preferably less than or equal to 0.015 %, and most preferably less than or equal to 0.011 %.

It is noted that glass according to this invention is often made via the known float process in which a tin bath is utilized. It will thus be appreciated by those skilled in the art that as a result of forming the glass on molten tin in certain exemplary embodiments, small amounts of tin or tin oxide may migrate into surface areas of the glass on the side that was in contact with the tin bath during manufacture (i.e., typically, float glass may have a tin oxide concentration of 0.05% or more (wt.) in the first few microns below the surface that was in contact with the tin bath).

In view of the above, glasses according to certain example embodiments of this invention achieve a neutral or substantially clear color and/or high visible transmission. In certain embodiments, resulting glasses according to certain example embodiments of this invention may be characterized by one or more of the following transmissive

optical or color characteristics when measured at a thickness of from about 1mm - 6mm (most preferably a thickness of about 0.219 inches; this is a non-limiting thickness used for purposes of reference only) (L_{ta} is visible transmission %):

TABLE 7: CHARACTERISTICS OF CERTAIN EXAMPLE EMBODIMENTS

	Characteristic	General	More Preferred	Most Preferred
5	L_{ta} (Ill. C, 2 deg.):	$\geq 75\%$	$\geq 80\%$	$\geq 85\%$
	%UV (Ill. C, 2 deg.):	$\leq 85\%$	$\leq 80\%$	$\leq 75\%$
	%TS (Ill. C, 2 deg.):	$\leq 90\%$	$\leq 87\%$	$\leq 85\%$
	%FeO (wt. %):	$\leq 0.020\%$	$\leq 0.015\%$	$\leq 0.011\%$
10	L^* (Ill. D65, 10 deg.):	90-100	n/a	n/a
	a^* (Ill. D65, 10 deg.):	-1.0 to +1.0	-0.60 to +0.60	-0.30 to +0.50
	b^* (Ill. D65, 10 deg.):	-1.0 to +1.5	-0.70 to +1.0	-0.30 to +0.40

As can be seen from Table 7 above, glasses of certain embodiments of this invention achieve desired features of fairly clear color and/or high visible transmission, while not requiring iron to be eliminated from the glass composition. This may be achieved through the provision of the unique material combinations described herein.

EXAMPLES

Example glasses of this invention may be made from batch ingredients using well known glass melting and refining techniques. The following approximate base glass batch was used for the Examples herein (note: the below-listed ingredients in the batch will add up to 100% by weight once oxides thereof are accounted for; thus, they need not add up to one hundred as raw materials):

	Batch Ingredient for Base Glass	Parts by Wt.
	sand	71.5
25	soda ash	23.7
	dolomite	18.32
	limestone	6.1

Epsom salt

0.9

In addition to the base glass batch materials above, the materials set forth below were present in the original batch(es) for the Examples (compound amounts given in wt. %). It is noted that Examples 1-8 are according to different example embodiments of this invention, while CA, CB and CC are Comparative Examples provided for purposes of comparison with Examples 1-8. In particular, Comparative Example A (CA) should be compared to Examples 1-3 of this invention since they all have the same amount of total iron, while Comparative Example B (CB) should be compared to Examples 4-5 of this invention since they all have the same total iron amount, and Comparative Example C (CC) should be compared to Examples 6-8 of this invention since they all have the same amount of total iron.

BATCH MATERIALS IN EXAMPLES 1-8 (IN ADDITION TO BASE BATCH)

Compound	CA	Ex. 1	Ex. 2	Ex. 3	CB	Ex. 4	Ex. 5	CC	Ex. 6	Ex. 7	Ex. 8
Fe ₂ O ₃ :	0.102	0.102	0.102	0.102	0.09	0.09	0.09	0.033	0.033	0.033	0.033
Er ₂ O ₃ :	0	0.06	0.08	0.11	0	0.086	0.08	0	0	0.10	0.09
CeO ₂ :	0	0.035	0.035	0.035	0	0.066	0.06	0	0.08	0.10	0.09
Nd ₂ O ₃ :	0	0	0	0	0	0	0	0.02	0.02	0.03	0.025

The batches were melted and glass formed using known techniques. Solar characteristics for the resulting Example glasses were as follows in the table below, with the below measurements taken after the melt and formation of the glass. It is noted that Lta (visible transmission%), UV transmission %, and %TS were measured using Ill. C, 2 degree observer, while transmissive L*, a* and b* color coordinates (CIE) were measured using Ill. D65, 10 degree observer. Moreover, Dom. λ stands for dominant wavelength, and Pe stands for excitation purity. All glass samples were about 0.219 inches thick (about 5.5-5.6 mm thick).

CHARACTERISTICS OF EXAMPLES 1-8 GLASSES

	Characteristic	CA	Ex. 1	Ex. 2	Ex. 3	CB	Ex. 4	Ex. 5	CC	Ex. 6	Ex. 7	Ex. 8
	% Lta	88.4	88.0	87.7	86.2	88.8	89.7	89.4	88.0	89.6	89.0	88.5
	% UV	74.5	68.9	74.8	73.6	76.9	65.9	66.4	76.2	65.9	63.2	63.6
5	% TS	79.6	83.1	81.3	79.8	79.2	84.5	84.0	79.5	84.9	86.0	84.9
	FeO (wt. %)	.0232	.011	.0177	.0191	.0254	.009	.0104	.023	.0079	.0042	.0065
	Dom. λ (nm)	498	562	487	487	493	573	564	492	537	566	581
	Pe %	0.64	0.37	0.24	0.22	0.9	0.48	0.27	0.96	0.25	0.07	0.07
	L*	95.5	95.2	95.1	94.4	95.7	95.8	95.7	93.6	95.9	95.6	95.4
10	a*	-1.54	-0.34	-0.18	-0.15	-1.49	-0.1	-0.21	-1.41	-0.72	0.09	-0.05
	b*	0.24	0.51	-0.12	-0.11	-0.15	0.58	0.39	-0.29	0.47	0.11	0.14

It can be seen from the above that glasses according to different embodiments of this invention (Examples 1-8) have one or more of the following example advantages over the Comparative Examples (CA, CB, and CC): (i) glasses according to Examples 1-8 had more neutral color than the respective Comparative Examples CA, CB and CC (it is noted that the Comparative Examples did not include erbium or cerium); (ii) glasses according to Examples 1-8 had less FeO (i.e., less iron in the ferrous state) than the respective examples (CA, CB and CC), even though the respective Examples and Comparative Examples for comparing therewith had the same amount of total iron; and/or (iii) glasses according to Examples 1-8 had lower excitation purity (Pe) than the respective Comparative Examples CA, CB and CC. High visible transmission (Lta) was maintained in Examples 1-8.

With respect to color, it can be seen for example that Example 1 was characterized by much more neutral a* color than CA (i.e., a* was closer to zero in Example 1 than in CA); compare a*=-0.34 of Example 1 with a*=-1.54 of Comparative

Example A (CA). In a similar manner, it can be seen for example that Example 4 had much more neutral a^* color than CB (i.e., a^* was closer to zero in Example 4 than in CB); compare $a^*=-0.1$ of Example 4 with $a^*=-1.49$ of Comparative Example B (CB). In a similar manner, it can be seen for example that Example 7 had much more neutral a^* color than CC (i.e., a^* closer to zero in Example 7 than in CC); compare $a^*=0.09$ of Example 7 with $a^*=-1.41$ of Comparative Example C (CC). The improved neutral color of example embodiments of this invention is a result of the unique material combinations used in glasses according to example embodiments of this invention.

It is noted that in any of Examples 1-8 above, the cerium oxide may be replaced with sodium nitrate in certain embodiments of this invention (see amounts in Tables 4-6 above). Certain examples according to other embodiments of this invention are set forth below (same base glass as above for other examples), where Examples 10-11 utilize sodium nitrate was used instead of or in addition to cerium oxide. It is noted that Examples 9-11 differed from Examples 1-8 above in that for Examples 9-11 each glass sample was only 0.161 inches thick.

BATCH MATERIALS IN EXAMPLES 9-11 (IN ADDITION TO BASE BATCH)

Compound	Ex. 9	Ex. 10	Ex. 11
Fe_2O_3 :	0.054	0.055	0.048
Er_2O_3 :	0.06	0	0
20 CeO_2 :	0.06	0.09	0
NaNO_3 :	0	0.5	0.78
Nd_2O_3 :	0	0	0

The above batches were melted and glass formed using known techniques. Solar characteristics for the resulting Example glasses were as follows in the table below, with the below measurements taken after the melt and formation of the glass.

CHARACTERISTICS OF EXAMPLES 9-11 GLASSES

	Characteristic	Ex. 9	Ex. 10	Ex. 11
	% Lta	90.43	91.32	90.75
	% UV	71.81	72.63	77.73
5	% TS	87.78	90.54	88.14
	FeO (wt. %)	0.0031	0.0007	0.0048
	Dom. λ (nm)	578	570	566
	Pe %	0.63	0.41	0.53
	L*	96.11	96.52	96.29
10	a*	0.09	-0.18	-0.36
	b*	0.67	0.5	0.67

As with the previous examples, it can be seen that Examples 9-11 have improved color (more neutral) and high visible transmission relative to the comparative examples, albeit reduced thickness. It is noted that Examples 9-11 utilized a smaller amount of total iron than Examples 1-8. Examples 9-11 illustrate that according to certain example embodiments of this invention, the glass may even have a visible transmission of at least 90% when at a reference thickness of about 0.161 inches.

The terms, and characteristics, of ultraviolet light transmittance (%UV), dominant wavelength, and excitation purity (i.e. % "purity", or Pe) are well understood terms in the art, as are their measurement techniques. Such terms are used herein, in accordance with their well known meaning, e.g., see U.S. Patent No. 5,308,805. In particular, ultraviolet transmittance (%UV) is measured herein using Parry Moon Air Mass = 2 (300 – 400 nm inclusive, integrated using Simpson's Rule at 10 nm intervals). Dominant wavelength (DW) is calculated and measured conventionally in accord with the aforesaid CIE Publication 15.2 (1986) and ASTM: E 308-90. The term "dominant wavelength" includes both the actual measured wavelength and, where applicable, its

calculated complement. Excitation purity (Pe or % "purity") is measured conventionally in accordance with CIE Publication 15.2 (1986) and ASTM: E 308-90.

Once given the above disclosure many other features, modifications and improvements will become apparent to the skilled artisan. Such features, modifications and improvements are therefore considered to be a part of this invention, the scope of which is to be determined by the following claims:

WHAT IS CLAIMED IS:

1. Glass comprising:

Ingredient	wt. %
SiO ₂	67 – 75 %
Na ₂ O	10 – 20 %
CaO	5 – 15 %
MgO	0 – 5 %
Al ₂ O ₃	0 – 5 %
K ₂ O	0 – 5 %
total iron (expressed as Fe ₂ O ₃)	0.01 to 0.30 %
erbium oxide	0.01 to 0.30 %
cerium oxide	0.005 to 0.30 %

wherein the glass has visible transmission of at least 75%, a transmissive a* color value of -1.0 to +1.0, and a transmissive b* color value of -1.0 to +1.5.

2. The glass of claim 1, wherein the glass comprises:

total iron (expressed as Fe ₂ O ₃)	0.02 to 0.20 %
erbium oxide	0.02 to 0.20 %
cerium oxide	0.01 to 0.18 %.

3. The glass of claim 2, wherein the glass comprises:

total iron (expressed as Fe ₂ O ₃)	0.03 to 0.15 %
erbium oxide	0.03 to 0.13 %
cerium oxide	0.03 to 0.12 %.

4. The glass of claim 1, wherein the glass further comprises from 0.005 to 0.15% neodymium oxide.
5. The glass of claim 4, wherein the glass further comprises from 0.010 to 0.050% neodymium oxide.
6. The glass of claim 1, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) \leq 0.20.
7. The glass of claim 1, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) \leq 0.15.
8. The glass of claim 1, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) \leq 0.13.
9. The glass of claim 1, wherein the glass further comprises less than or equal to 0.020 % FeO.
10. The glass of claim 1, wherein the glass further comprises less than or equal to 0.015 % FeO.
11. The glass of claim 1, wherein the glass further comprises less than or equal to 0.011 % FeO.
12. The glass of claim 1, wherein the glass has a visible transmission of at least 80%.

13. The glass of claim 1, wherein the glass has a visible transmission of at least 85%.

14. A method of making glass, the method comprising:
providing a glass batch comprising:

Ingredient	wt. %
SiO ₂	67 – 75 %
Na ₂ O	10 – 20 %
CaO	5 – 15 %
MgO	0 – 5 %
Al ₂ O ₃	0 – 5 %
K ₂ O	0 – 5 %
total iron (expressed as Fe ₂ O ₃)	0.01 to 0.30 %
erbium oxide	0.01 to 0.30 %
cerium oxide and/or a nitrate	0.005 to 2.0 %
neodymium oxide	0 to 0.15 %

melting the batch and forming a resulting glass that has visible transmission of at least 75%, a transmissive a* color value of -1.0 to +1.0, and a transmissive b* color value of -1.0 to +1.5.

15. The method of claim 14, wherein the nitrate comprises at last one of potassium nitrate (KNO₃) and sodium nitrate (NaNO₃), and the batch comprises:

total iron (expressed as Fe ₂ O ₃)	0.02 to 0.20 %
erbium oxide	0.02 to 0.20 %

cerium oxide 0.01 to 0.18 %

neodymium oxide 0 to 0.15 %.

16. The method of claim 14, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) ≤ 0.20 .

17. The method of claim 14, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) ≤ 0.15 .

18. The method of claim 14, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) ≤ 0.13 .

19. The method of claim 14, wherein after the melting the glass comprises less than or equal to 0.020 % FeO.

20. The method of claim 19, wherein the glass comprises less than or equal to 0.015 % FeO.

21. The method of claim 20, wherein the glass comprises less than or equal to 0.011 % FeO.

22. The method of claim 14, wherein the glass has a visible transmission of at least 80%.

23. Glass comprising:

total iron (expressed as Fe_2O_3) 0.01 to 0.30 %

erbium oxide 0.01 to 0.30 %

cerium oxide 0.005 to 0.30 %.

24. The glass of claim 23, wherein the glass has visible transmission of at least 75%, a transmissive a^* color value of -1.0 to $+1.0$, and a transmissive b^* color value of -1.0 to $+1.5$.

25. The glass of claim 23, wherein the glass comprises:

total iron (expressed as Fe_2O_3)	0.02 to 0.20 %
erbium oxide	0.02 to 0.20 %
cerium oxide	0.01 to 0.18 %.

26. The glass of claim 23, wherein the glass comprises:

total iron (expressed as Fe_2O_3)	0.03 to 0.15 %
erbium oxide	0.03 to 0.13 %
cerium oxide	0.03 to 0.12 %.

27. The glass of claim 23, wherein the glass further comprises from 0.005 to 0.15% neodymium oxide.

28. The glass of claim 23, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) ≤ 0.15 .

29. The glass of claim 23, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) ≤ 0.13 .

30. The glass of claim 23, wherein the glass further comprises less than or equal to 0.015 % FeO.

31. The glass of claim 23, wherein the glass has a visible transmission of at least 85%.

32. A method of making glass, the method comprising providing a glass batch comprising:

total iron (expressed as Fe_2O_3):	0.01 to 0.30 %
erbium oxide:	0.01 to 0.30 %
cerium oxide and/or a nitrate:	0.005 to 2.0 %, and

using the glass batch to make glass.

33. The method of claim 32, wherein the batch comprises a nitrate in the amount (wt. %) of from 0.005 to 2.0%.

34. The method of claim 33, wherein the nitrate comprises at least one of potassium nitrate (KNO_3) and sodium nitrate (NaNO_3).

35. The method of claim 34, wherein the batch comprises at least one of potassium nitrate (KNO_3) and sodium nitrate (NaNO_3) in a total amount of from 0.2 to 1.5%.

36. The method of claim 32, wherein the glass has visible transmission of at least 75%, a transmissive a^* color value of -1.0 to $+1.0$, and a transmissive b^* color value of -1.0 to $+1.5$.

37. The method of claim 32, wherein the glass comprises:

total iron (expressed as Fe_2O_3)	0.02 to 0.20 %
--	----------------

erbium oxide	0.02 to 0.20 %
cerium oxide	0.01 to 0.18 %.

38. The method of claim 32, wherein the glass comprises:

total iron (expressed as Fe_2O_3)	0.02 to 0.20 %
erbium oxide	0.02 to 0.20 %
neodymium oxide	0 to 0.15 %.

39. The method of claim 32, wherein glass comprises from 0.005 to 0.15% neodymium oxide.

40. The method of claim 32, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) ≤ 0.15 .

41. The method of claim 32, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) ≤ 0.13 .

42. The method of claim 32, wherein the glass further comprises less than or equal to 0.015 % FeO.

43. The method of claim 32, wherein the glass has a visible transmission of at least 85%.

44. Glass comprising:

total iron (expressed as Fe_2O_3)	0.01 to 0.30 %
erbium oxide	0.01 to 0.30 %.

45. The glass of claim 44, further comprising:
- | | |
|--|-----------------|
| total iron (expressed as Fe_2O_3) | 0.02 to 0.20 % |
| erbium oxide | 0.02 to 0.20 %. |
46. The glass of claim 44, further comprising:
- | | |
|--|-----------------|
| total iron (expressed as Fe_2O_3) | 0.03 to 0.15 % |
| erbium oxide | 0.03 to 0.13 %. |
47. The glass of claim 44, further comprising from 0.005 to 0.15 % neodymium oxide.
48. The glass of claim 44, further comprising from 0.010 to 0.050 % neodymium oxide.
49. The glass of claim 44, further comprising from 0.005 to 0.30% cerium oxide.
50. The glass of claim 44, wherein the glass has visible transmission of at least 75%, a transmissive a^* color value of -1.0 to $+1.0$, and a transmissive b^* color value of -1.0 to $+1.5$.
51. The glass of claim 50, wherein the glass has a visible transmission of at least 85%.
52. The glass of claim 44, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) ≤ 0.15 .

53. The glass of claim 44, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) ≤ 0.13 .

54. The glass of claim 44, wherein the glass further comprises less than or equal to 0.015 % FeO.

55. The glass of claim 44, further comprising:

SiO_2	67 – 75 %
Na_2O	10 – 20 %
CaO	5 – 15 %
MgO	0 – 5 %
Al_2O_3	0 – 5 %
K_2O	0 – 5 %.

56. Glass comprising:

neodymium oxide	0.005 to 0.15%, and
erbium oxide	0.01 to 0.30 %.

57. The glass of claim 56, further comprising:

total iron (expressed as Fe_2O_3)	0.02 to 0.20 %
erbium oxide	0.02 to 0.20 %.

58. The glass of claim 56, further comprising from 0.005 to 0.30% cerium oxide.

59. The glass of claim 56, wherein the glass has visible transmission of at least 75%.

60. The glass of claim 59, wherein the glass has a transmissive a^* color value of -1.0 to $+1.0$, and a transmissive b^* color value of -1.0 to $+1.5$.

61. The glass of claim 56, wherein the glass has a visible transmission of at least 85%.

62. The glass of claim 57, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) ≤ 0.15 .

63. Glass comprising:

total iron (expressed as Fe_2O_3)	0.01 to 0.30 %
neodymium oxide	0.005 to 0.15 %.

64. The glass of claim 63, further comprising

total iron (expressed as Fe_2O_3)	0.02 to 0.20 %
erbium oxide	0.02 to 0.20 %.

65. The glass of claim 63, further comprising from 0.005 to 0.30% cerium oxide.

66. The glass of claim 63, wherein the glass has visible transmission of at least 75%, a transmissive a^* color value of -1.0 to $+1.0$, and a transmissive b^* color value of -1.0 to $+1.5$.

67. The glass of claim 63, wherein the glass has a visible transmission of at least 85%.

68. The glass of claim 63, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) ≤ 0.15 .

69. The glass of claim 63, wherein the glass further comprises less than or equal to 0.015 % FeO.

70. The glass of claim 63, further comprising:

SiO_2	67 – 75 %
Na_2O	10 – 20 %
CaO	5 – 15 %
MgO	0 – 5 %
Al_2O_3	0 – 5 %
K_2O	0 – 5 %.

71. The glass of claim 1, wherein the glass has a visible transmission of at least 90% when having a reference thickness of from 5.5 to 5.6 mm.

72. The glass of claim 23, wherein the glass has a visible transmission of at least 90% when having a reference thickness of from 5.5 to 5.6 mm.

73. The glass of claim 44, wherein the glass has a visible transmission of at least 90% when having a reference thickness of from 5.5 to 5.6 mm.

74. Glass comprising:

total iron (expressed as Fe_2O_3)	0.01 to 0.10 %
cerium oxide	0.01 to 0.18 %

wherein the glass has a visible transmission of at least 85%, a transmissive a^* color value of -1.0 to $+1.0$, and a transmissive b^* color value of -1.0 to $+1.5$.

75. The glass of claim 74, wherein the glass has a redox value ($\text{FeO}/\text{Fe}_2\text{O}_3$) ≤ 0.15 .
76. The glass of claim 74, further comprising from 0.02 to 0.20 % erbium oxide.
77. The glass of claim 74, wherein the glass was made using a batch comprising from 0.005 to 2.0 % of nitrate.
78. The glass of claim 77, wherein the nitrate comprises NaNO_3 .

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/02388

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C3/087 C03C3/095

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 13993 A (VYSOKA SKOLA CHEM TECH ; RADA MIROSLAV (CZ); SASEK LADISLAV (CZ)) 26 May 1995 (1995-05-26) example 5	55,70
A	---	1-22,71
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 08, 30 June 1999 (1999-06-30) & JP 11 060269 A (TOYO GLASS CO LTD), 2 March 1999 (1999-03-02) abstract paragraph [0002]	55,70
A	US 5 264 400 A (NAKAGUCHI KUNIO ET AL) 23 November 1993 (1993-11-23) column 3, line 1 - line 15 column 3, line 28 - line 32; table 1 --- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

23 May 2003

Date of mailing of the international search report

07 07 2003

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INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/US 03/02388

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 116 699 A (NIPPON SHEET GLASS CO LTD) 18 July 2001 (2001-07-18) example 5 abstract ---	
P,A	US 6 498 118 B1 (HALL JR DAVID R ET AL) 24 December 2002 (2002-12-24) claim 18; table 6 ---	
P,A	WO 02 081395 A (GUARDIAN INDUSTRIES) 17 October 2002 (2002-10-17) example 2 abstract -----	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/02388

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos..
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 23-54, 56-69, 72-74
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

Continuation of Box I.2

Claims Nos.: 23-54,56-69,72-74

Present claims 23-54, 56-69 and 72-74 relate to an extremely large number of possible glass compositions. Support within the meaning of Article 6 PCT and / or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compositions claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts related to compositions based on a soda-lime-silica glass (see the description page 4, lines 13-14) and including iron.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/02388

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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